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Empirical study of the characteristics of current-state organic bulk heterojunction solar cells*

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Abstract. We studied and compared the reported characteristics of 22 different bulk heterojunction organic solar cells fabricated and characterized by different research institutes. We only considered bulk heterojunction solar cells where both the acceptor (the n-type) and the donor (the p-type) are organic. All cells were characterized under illumination with the standard A.M. 1.5 spectrum and an intensity of 100 mW/cm^2. The material properties (the highest occupied (HOMO) and lowest unoccupied molecular orbital (LUMO) of donor and acceptor) and the device characteristics (the open circuit voltage V_{oc}, the short circuit current density J_{sc}, the fill factor FF and the efficiency) are compared and related to each other. One finding is that not the V_{oc}, but the J_{sc} is the limiting factor for obtaining a high efficiency with the current state of technology. Also an empirical threshold of 0.2 eV is found between the LUMO's of the donor and acceptor, necessary for exciton dissociation. There has long been a debate about the origin of the V_{oc}. In recent literature, it is proposed that the V_{oc} is not related with the work function difference of the contacts, but with the energy difference between the LUMO of the acceptor, and the HOMO of the donor (called 'the interface bandgap'). A relation between the V_{oc} and the energy levels of donor and acceptor is searched from our empirical study.

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1 Introduction

Photovoltaic solar cells based on conjugated polymer/fullerene compounds are promising candidates for solar energy conversion. Organic plastic cells have the potential for cost effectiveness and mechanical flexibility. A bulk heterojunction solar cell consist of a nanoporous interpenetrating network of an n-type (e.g. fullerene derivatives) and a p-type (semi)conductor (e.g. conjugated polymer), sandwiched between two electrodes with different work functions.

For this empirical research, we studied and compared the reported characteristics of different organic solar cells fabricated and characterized by different research institutes [1–21]. We only considered solar cells where both the acceptor (the n-type) and the donor (the p-type) are organic solid state materials. Organic-inorganic hybrid cells, liquid dye sensitized solar cells and tandem cells were omitted for this study. For each donor-acceptor material combination, only the cell with the highest reported efficiency was taken into account. The cells were characterized under illumination with the standard A.M. 1.5 spectrum and an intensity of 100 mW/cm^2. Some cells [3,7,11,12] were characterized with a lower intensity (∼80 mW/cm^2). We adapted the J_{sc} linearly of those cells to compare them with the cells characterized at 100 mW/cm^2. No corrections were made for the V_{oc} or FF.

This resulted in experimental data of 22 bulk heterojunction organic solar cells, of which the oldest data was published in 2002. In a bulk heterojunction solar cell, the active layer consists of a nanoporous interpenetrating network of the donor and the acceptor. As expected, no bilayer cells were found with a higher efficiency as their bulk heterojunction counterpart. All 22 cells use as transparent hole-contact Indium Tin Oxide (ITO). As electron contact, different materials can be used. Al is used in most cases (18 cells), Au and Ag are each used in 2 cells.

The best standard efficiency published for organic solar cells is at this time 4.9% + / − 0.2% for an ITO / PEDOT:PSS / P3HT:PCBM (1:1) / LiF / Al – cell [12]. This cell has an active area of 0.19 cm^2, and is characterized at 80 mW/cm^2 by an open circuit voltage V_{oc} of 0.64 V, a short circuit current density J_{sc} of 11.1 mA/cm^2, and a fill factor FF of 54%.

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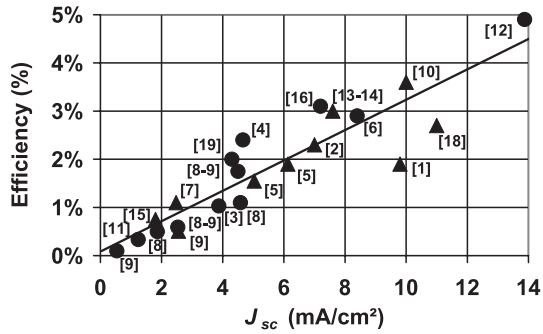

Fig. 1. The short circuit current density J_{sc} plotted versus the power conversion efficiency η of the studied solar cells. The circles and triangles represent respectively cells where PCBM is the acceptor material and where PCBM is not the acceptor material. The data-points are labelled with their respective references. The straight line is the linear fit. We see a clear linear correlation: an increase of 1 mA/cm^2 results roughly in an efficiency gain of 1/3 of a percent absolute.

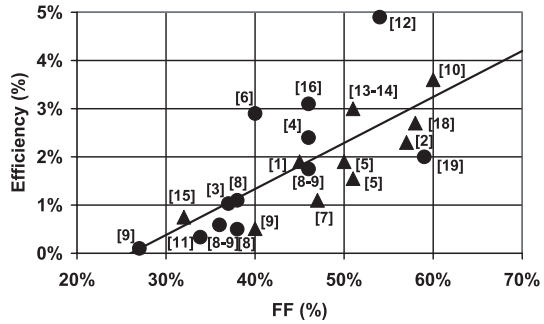

Fig. 2. The fill factor FF plotted versus the power conversion efficiency η of the studied solar cells. The circles and triangles represent respectively cells where PCBM is the acceptor material and where PCBM is not the acceptor material. The data-points are labelled with their respective references. The straight line is the linear fit.

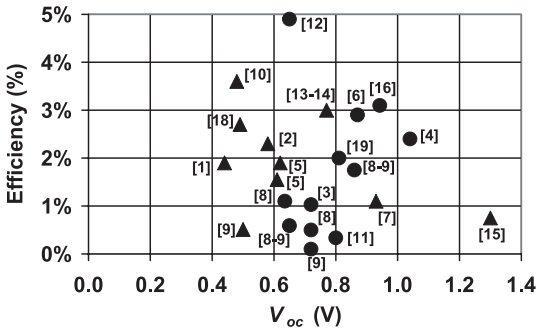

Fig. 3. No correlation is found between the open circuit voltage V_{oc} and the power conversion efficiency η of the studied solar cells. The circles and triangles represent respectively cells where PCBM is the acceptor material and where PCBM is not the acceptor material. The data-points are labelled with their respective references.

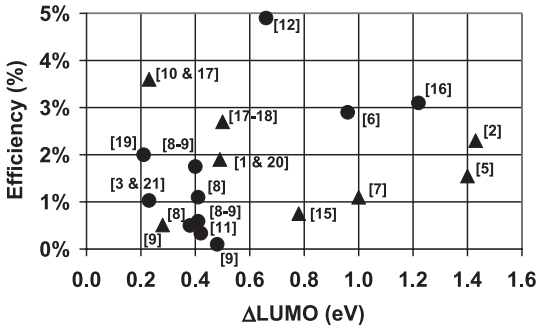

Fig. 4. The efficiency as a function of the energy difference between the LUMO's of the donor and the acceptor. The circles and triangles represent respectively cells where PCBM is the acceptor material and where PCBM is not the acceptor material. The data-points are labelled with their respective references. An empirical threshold of 0.2 eV is found between the LUMO's of the donor and acceptor, necessary for exciton dissociation.

2 Results

The power conversion efficiency η of a solar cell is given by the formula:

$$\eta = FF \cdot \frac{V_{oc} \cdot J_{sc}}{P_{in}} \tag{1}$$

where V_{oc} is the open circuit voltage, J_{sc} the short circuit current density, FF the fill factor and P_{in} the incident solar light power. When we plot the measured characteristics of the different cells versus the efficiency (Figs. 1 and 2), we see a clear linear correlation for the short circuit current density J_{sc} (and to a lesser extend for the fill factor FF). An increase of 1 mA/cm^2 results roughly in an efficiency gain of 1/3 of a percent absolute. However, this linear correlation is not seen for the efficiency versus the open circuit voltage V_{oc} (Fig. 3). This empirical result indicates that, with the current state of the technology, the current is the limiting factor for reaching higher efficiencies, and not the V_{oc}. The average V_{oc} of the cells, i.e. 0.75 V, is already satisfying high. Where there is no clear relationship between the V_{oc} and the efficiency, this relation is present for the J_{sc}. Of course, reaching higher voltages will increase the efficiency of the solar cells, but a higher efficiency gain can be obtained by focussing on reaching higher currents, which is an important bottleneck for the breakthrough of organic solar cells.

The absorption of a photon leads to the creation of an exciton (a bound electron-hole pair) in the donor of a bulk heterojunction solar cell. For the charge carriers to contribute to the current, the exciton needs to be dissociated into an electron and a hole before recombination happens. The exciton is dissociated at the discontinuous potential drop at the interface between donor and acceptor. The electron is transferred to the electron acceptor due to its high electron affinity.

A necessary condition for exciton dissociation is that the difference between the LUMO's of the donor and acceptor is higher than the exciton binding energy. Although the value of the exciton binding energy in different materials is often a subject of discussion, values between 0.1 eV and 2 eV are published [22]. Figure 4 shows the efficiency

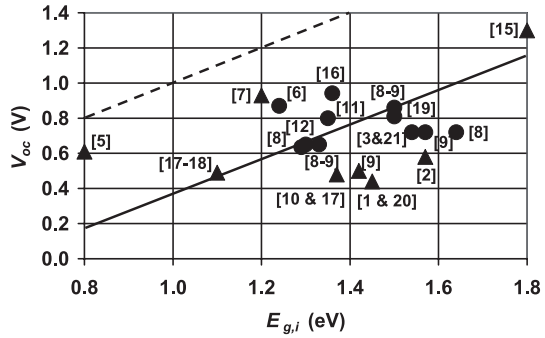

Fig. 5. The open circuit voltage V_{oc} as a function of the interface bandgap $E_{g,i}$ of the studied solar cells. The circles and triangles represent respectively cells where PCBM is the acceptor material and where PCBM is not the acceptor material. The data-points are labelled with their respective references. The dotted line indicates the limit for the V_{oc}. The full line is not a fit, but represents slope 1.

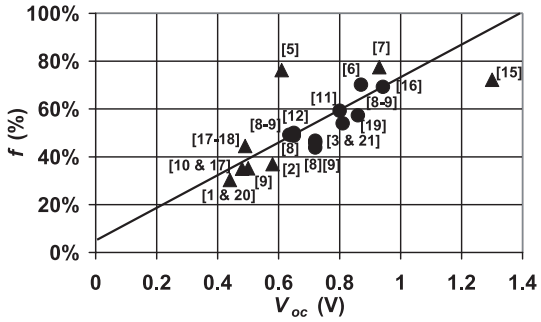

Fig. 6. The voltage factor f as a function of the open circuit voltage V_{oc} of the studied solar cells. The circles and triangles represent respectively cells where PCBM is the acceptor material and where PCBM is not the acceptor material. The data-points are labelled with their respective references. The straight line is the linear fit.

as a function of the energy difference between the LUMO's of the donor and the acceptor. Most energy differences are lying between 0.2 eV and 0.5 eV, although some even reach 1 eV and higher. If the difference between the LUMO's is higher than necessary for the exciton dissociation, the electron loses useful energy that can't contribute any more to the output power, although this is not clear from Figure 4. An empirical threshold of 0.2 eV is found between the LUMO's of the donor and acceptor. Because no working cells were found below that threshold, a minimal difference of 0.2 eV between the LUMO's can be considered as necessary for exciton dissociation.

According to the metal-insulator-metal (MIM) model, the open circuit voltage V_{oc} should reflect the difference between the workfunctions ϕ of the metal electrodes. Because most of our studied solar cells use ITO (ϕ = 4.7–4.9 eV) and Al (ϕ = 4.3 eV) as contacts, a maximum V_{oc} of 0.4–0.6 V is expected. In reality, the V_{oc} of organic bulk heterojunction solar cells is usually higher, and quite independent of the metal top electrode [23,24]. The average V_{oc} of our cells amounts to 0.75 V. One cell [15] even reaches a V_{oc} of 1.3 V with Al and ITO-contacts. The distance between the HOMO of the donor and the LUMO of the acceptor has to be considered as the thermodynamic limitation for the V_{oc}. This value is often called the interface bandgap $E_{g,i}$. Considering this limit, a linear relationship exists between V_{oc} and $E_{g,i}$, which was recently demonstrated for cells with different donors and PCBM as acceptor [25]. However, the V_{oc}–$E_{g,i}$-plot of our studied cells (Fig. 5) does not show a linear relationship. This can be explained by the difference in the state of the production technology for each cell.

If we consider the interface bandgap $E_{g,i}$ as the limit for the open circuit voltage V_{oc}, the voltage factor f is given by:

$$f = \frac{q \cdot V_{oc}}{E_{g,i}}. \quad (2)$$

Because of loss factors (e.g. recombination), f can not reach 1. In Figure 6, we see a linear relationship between f and V_{oc}, meaning that the higher the V_{oc}, the more efficiently energy of the bandgap is used. The voltage factor for highly efficient inorganic solar cells (where the bandgap E_g has to be considered instead of the interface bandgap $E_{g,i}$) with e.g. active materials CdTe, Si and GaAs is respectively 58%, 63% and 70% [26]. Compared with those values, the voltage factor for organic bulk heterojunction solar cells already reaches satisfying values.

3 Conclusions

We studied and compared the reported characteristics of 22 different bulk heterojunction organic solar cells fabricated and characterized by different research institutes. We found that not the V_{oc} , but the J_{sc} is the limiting factor for obtaining a high efficiency with the current state of technology. Also an empirical threshold of 0.2 eV was found between the LUMO's of the donor and acceptor, necessary for exciton dissociation. Because of the different states of technology for the cells, a relation between the V_{oc} and the interface bandgap was not found.

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